

STCG Subcon Subgroup Meeting Minutes

April 17, 2001

Welcome/Announcements (Arlene Tortoso)

Arlene welcomed everyone. She mentioned that Mike Thompson was arranging a May 9 briefing by SCFA on caps and covers. (That briefing has since been cancelled due to lack of travel funds.) She also mentioned that the STCG Management Council meeting is scheduled for May 17. There was a Carbon Tet ITRD meeting on April 11 that was focused on what activities the ITRD Program could support at Hanford.

Jim Hanson mentioned that comments on the Sitewide S&T Assessment were due by April 16. The path forward is to see what comments are received, and possibly do some follow-on S&T roadmaps. Gordon Rogers said he was surprised that there was no reference to an ongoing DOE-HQ study on the impacts of low-dose exposures to the public. He agreed to send his comments to Wayne Johnson. Gordon also said that he thinks the assessment is an excellent piece of work and we need to get funding to carry out the recommendations that are presented.

Arlene mentioned that a proposal titled "Delineation and Remediation of DNAPLs in the Vadose Zone Using Advanced Cone Penetrometer Tools" was sent to SCFA on April 11 for funding through the Quick Win deployment call for proposals. This proposal was jointly prepared by BHI and PNNL. It presents plans to quickly deploy innovative technologies to address high-priority needs at the Hanford Site associated with characterization and remediation of the carbon tetrachloride plume.

Jerry White mentioned that Gerald Boyd is having the November 1998 Environmental Management R&D Program Plan rewritten with a 5-10 year focus. Jerry is on the team that is working on this assignment, and he promised to share drafts with the Subgroup. SCFA is also developing a new strategic plan for the next 5-10 years. They presented a preliminary draft at the SCFA Mid-Year Review, and it had lots of holes. They are now trying to revamp it based on the comments they received. It will determine the directions/focus on what to fund in the near term, but not the details. Comments on the preliminary draft were due on April 17. Caps and covers is one key theme for the next 5-10 years. A new draft was to be ready by the end of April to show Gerald.

Mike Thompson mentioned that a group from Idaho was here at Hanford looking for comments and support for their Complex-wide groundwater/vadose zone roadmap. This roadmap is at a higher level than Hanford's and contains more general research needs. The activity may be zeroed out in the President's budget.

Review Minutes from Last Meeting (Facilitator)

The facilitator reviewed the minutes from the February 13, 2001 meeting. No changes were

requested.

Chromium Behavior in the S-SX Tank Farm – Geochemical and Transport Mechanisms (John Zachara)

John's S&T team linked up with Tony Knepp's S-SX tank farm team as part of the DQO process for SX-108, 109, and 115. They developed objectives to focus on chromium geochemical behavior, as well as cesium and technetium. John has also built strong relationships with the EMSP projects in this area.

During the Manhattan Project, dichromate was used as an oxidant to adjust the valence states of uranium and plutonium in the REDOX process. About 50% of the unreduced dichromate went into the supernatant phase, where its concentration was about 0.4M. It has been estimated that about 2500 kg of chromium were released to the environment in the tank farms. There was little retardation of the chromium in the 100 Areas, and John's team wanted to see if this was true for the tank farms as well. The scientific issues they focused on for chromium include:

- Cr(VI)/Cr(III) ratios in REDOX waste
- Cr(VI) as a HLW indicator in groundwater
- Cr(VI) retardation extent and mechanism
- Transport behavior vis-à-vis other mobiles
- Remobilization potential of sorbed chromium

It turned out that the technetium is not retarded, but the chromium is somewhat. The tanks had high concentrations of hydroxide and aluminate, and it appeared that a reduction mechanism was occurring in the tank farms that could contribute to retardation of chromium. John's team asked the EMSP researchers to help with the calculations on four samples from tank farm sediments.

The results of the calculations showed that there was a significant reduction of Cr(VI) to Cr(III) in the tank farms. The researchers determined that the Cr(III) was mainly associated with biotite and ilmenite in the sediments. Both of these are minerals that contain ferrous iron, which is a strong reductant of Cr(VI). Almost all the Cr(VI) was solubilized from the sediments when leached with water. The typical REDOX waste was high base, high salt, and aluminum. Their conceptual model said that the reduction of Cr(VI) to Cr(III) was done by the tank farm sediments. Some of the quartz-rich sediments in the tank farm soils look like poorly ordered zeolites. There was no retardation of selenium and technetium, but approximately 50% of the Cr(VI) was immobilized in the sediments. Molybdenum was retarded even more than chromium. The cesium was retarded by ion exchange processes rather than electron transfer processes.

The findings of John's team's research showed:

- Approximately 30-60% of the Cr(VI) present in REDOX tank waste was immobilized in sediments as a Cr(III) precipitate.
- In situ mapping showed Cr(III) associated with biotite and ilmenite.
- Laboratory study indicated that the reduction reaction was facilitated by hydroxide.
- Kinetic controls on reaction extent.

The contaminants in the tank farm vadose zone reached depth rapidly. Then the kinetic processes occurred – base dissolution with base-catalyzed reduction of Cr(VI), driven by the base reaction with the minerals in the soil to neutralize. The Cr(III) should remain as is without any strong oxidant present.

The research team can develop a strategy to minimize transport of an individual contaminant, but it is very difficult to do so for the entire combination by using different sluicing compositions. Then there is the issue of what gets sent to the vitrification plant. Dirk Dunning suggested sulfide immobilization of the metals first. Cesium will never go far enough to be of concern, but technetium could. Long-term control of water influx is needed. Ed Thornton stated that the potential application of in situ gaseous reduction to immobilization of technetium under the tanks is currently being investigated in laboratory experimental studies.

Mark Freshley mentioned that John Zachara was scheduled to talk to the Groundwater/Vadose Zone Expert Panel on this work in the near future. About 50% of John's funding for this work came from the Groundwater/Vadose Zone Integration Project, and about half came from the Environmental Management Science Program (EMSP).

Cr(VI)-Enriched Calcite – Long-Term Source for Chromate in the Hanford Vadose Zone and Unconfined Aquifer? (Ed Thornton)

Ed's work was funded mainly by EMSP, but SCFA funded his earlier work.

Hexavalent chromium is an important groundwater contaminant in the 100 Areas at Hanford. When the plutonium production reactors were operating, sodium dichromate stock solution was added to the cooling water as a corrosion inhibitor. It was delivered in rail cars to the 100-D Area transfer stations, for example, and then distributed via underground pipes to the water treatment plants associated with the reactors. Chromate stock or chromate-treated reactor cooling water is the primary source of the groundwater contamination.

Cr(VI) is very persistent, despite its high mobility. It is very soluble as the CrO_4^{2-} anion, while Cr(III) is essentially insoluble. After 30 years, however, hexavalent chromium is still present in the soil at several of the 100-Area water treatment plant sites, suggesting that a retardation effect is present. A yellowish coloration or coating is common in Hanford Site Cr(VI)-contaminated soils, suggesting that transport may be limited by the solubility of specific Cr(VI)-bearing minerals. Characterization activities have recently been conducted on a yellow mineral product found at the 190-D site in the 100-D Area. This material was determined to be Cr(VI)-enriched calcite with barium chromate inclusions.

Ed's conclusions are:

- Cr(VI) may be present in the vadose zone as Cr(VI)-enriched calcite and as barium chromate (BaCrO_4).
- The apparent retardation of Cr(VI) in the vadose zone and unconfined aquifer may be due to the equilibrium distribution of Cr(VI) between calcite and pore fluids.

The implications for remediation are:

- Cr(VI) contamination in the vadose zone may reside in calcite cement in sediments.
 - Possibly released during periodic influxes or infiltration of fresh water.
 - Further research needs to be undertaken to evaluate the potential effectiveness of in situ treatment approaches such as ISGR when Cr(VI) is contained in minerals such as calcite.
- If the apparent retardation of Cr(VI) in the unconfined aquifer is due to uptake and release of Cr(VI) by calcite, then:
 - Aquifer remediation by the pump-and-treat approach may be difficult to achieve.
 - Groundwater contamination containment by ISRM coupled with vadose zone source control by ISGR may be more effective in the long term.

Dennis Faulk noted that a couple more wells are being drilled in the 100 Areas. As the project is going through the DQO process, they should ask what is happening in the aquifer and near the aquifer.

S&T Needs for the 618-10 and 618-11 Burial Grounds (Mike Truex)

Mike presented the following proposed new S&T needs for the 618-10 and 618-11 burial grounds:

- **RL-SS48 Remote Handling During Excavation Activities** – This statement describes the need for removing material using remote-handling techniques due to high dose rate conditions or difficult access (e.g., caissons). The caissons and drum storage units are discussed as specific waste types requiring special handling.
- **RL-SS49 Contamination Control During Excavation Activities** – This statement describes the need for controlling the spread of TRU and high dose rate contaminated material during all phases of the excavation process and the need for appropriate shielding for these materials.
- **RL-SS50 Waste Segregation and Packaging for TRU and High Dose Rate Contaminated Material** – This statement describes the need to segregate and volume reduce TRU waste while packaging the waste for transport away from the burial ground. Specific issues include the need to handle different sizes and shapes of contaminated materials, the need for remote handling of high dose rate material, and the need for contamination control during the segregation and packaging operations.

He also presented the following modified needs:

- **RL-SS18 Improved Detection and Segregation of TRU Waste (Debris)** – This need was modified to specifically discuss field characterization for identification and initial segregation of TRU and high dose rate contaminated material during excavation operations.
- **RL-SS10 Improved Technologies for Detection/Delineation of Burial Ground Contents and Waste Site Boundaries** – This need was modified to include examples of waste types in the 618-10/11 burial grounds (e.g., caissons) that need to be characterized prior to excavation.

BHI is talking to other sites with similar burial grounds and caissons. Dennis Faulk stated that Hanford is at least 10 years away from excavation of caissons. Jerry White said BHI is looking

to see if there are multiple site benefits. Remedial design information is needed by about 2005. Dirk Dunning said that the waste must be characterized for shipment to WIPP. We need video cameras for high-activity environments, gamma cameras, and shielded equipment for workers.

The needs statements were distributed electronically for review by the Subgroup members. Comments were due to Scott Petersen by May 15. The comments received will be discussed at the June meeting and the needs will be endorsed for transmittal to SCFA.

Attendees

Jim Bush (PNNL)
Dirk Dunning (Oregon)
Linda Fassbender (PNNL)
Dennis Faulk (EPA)
Mark Freshley (PNNL)
John Fruchter (PNNL)
Judit German-Heins (Nez Perce Tribe) – participated by phone
Dib Goswami (Ecology)
Jim Hanson (DOE-RL)
Ron Jackson (BHI)
Ken Kapsi (DOE-RL)
Wade Riggsbee (Yakama Nation)
Gordon Rogers (HAB)
Jeff Serne (PNNL)
Mike Thompson (DOE-RL)
Ed Thornton (PNNL)
Arlene Tortoso (DOE-RL)
Mike Truex (PNNL)
Jerry White (BHI)
Rob Yasek (DOE-ORP)
John Zachara (PNNL)

Next Meeting

The next Subcon Subgroup meeting was scheduled for June 19. Potential agenda items include:

- Proposed New and Modified S&T Needs for the 618-10 and 618-11 Burial Grounds
- Carbon Tet Project Quick Wins
- NETL